ON THE THERMAL STABILITY AND THERMAL DECOMPOSITION KINETICS OF SOME MONO- AND DISUBSTITUTED FURAN-2,3-DIONES

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Abstract

The thermal behaviour of some compounds derived from 5-phenylfuran-2,3-dione was studied.

The thermoanalytical data relating to the decomposition steps and intermediates were completed with mass spectrometric analysis and infrared spectroscopy results. For some of the investigated reactions, the kinetic and structural data correlated satisfactorily.

Introduction

Our earlier research on the thermal stability of organic compounds [1] has now been continued with a study of the thermal behaviour of 5-phenylfuran-2,3-dione and three substituted derivatives. The interest in such an investigation is due to the structure of the basic compound, which is structurally related with ascorbic acid and to the changes induced by substitution, which suggest several possible modes of bond breaking and thus initiation of thermal decomposition.

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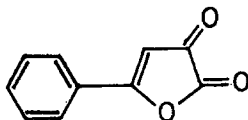
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This investigation was also designed to identify the decomposition interme-
diates, establish the temperature ranges of their thermal stability, and evaluate
the nonisothermal kinetic parameters associated with the decomposition. These
values allow simulation of the thermogravimetric curve. To the best of our
knowledge, such a kinetic investigation of furandiones in the solid state has not
previously been performed, earlier studies relating to thermal decomposition in
solution or to gas-phase pyrolysis [2–5].

Experimental

Powders of 5-phenylfuran-2,3-dione, 5-tolylfuran-2,3-dione, 5-(4-chlor-
phenyl)-furan-2,3-dione and 4-benzoyl-5-phenylfuran-2,3-dione synthetized by
procedures described in the literature [6] were used.

The TG, T, DTG and DTA heating curves were recorded with a type C deri-
vatograph (MOM, Budapest) in static air atmosphere, at heating rates in the
range 2.5–5 K min^{-1}.

For evaluation of the non-isothermal kinetic parameters of the thermal de-
composition, in the framework of the 'reaction order' model, three methods
were applied: those of Coats and Redfern [7], Flynn and Wall [8] and Ur-
banovici and Segal [9] (the modified Coats-Redfern method).

The experimental data were processed with a program written in Basic [10]
and run on an IBM-PS/2 computer. The same program allowed regeneration of
the TG curves in the coordinates degree of conversion α vs. $T°C$, using the de-
termined values for the non-isothermal kinetic parameters and fitting the
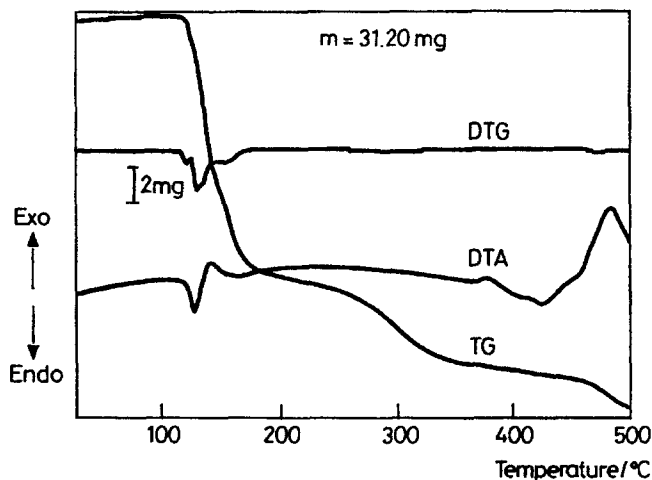experimental points to them.

Fig. 1 TG, DTG and DTA curves of 5-phenyl-2,3-furandione. m=sample mass

The mass spectra of the gaseous products evolved on heating of the investigated compounds at low pressure (10^{-6} mbar) were obtained with a Type SE, double-focusing mass spectrometer (VG – Analytical, Manchester).

In order to establish whether the first decomposition step occurs in the solid or in the liquid phase, a Boetius microscope (VEB, Dresden) equipped with a heating system was used.

The results were corroborated with information obtained from the IR spectra of the investigated compounds and their thermal decomposition intermediates [11].

Results and discussion

Thermal decomposition of 5-phenylfuran-2,3-dione

As can be seen from Fig. 1, the melting of this compound occurs at 110°C, while its thermal decomposition begins at practically the same temperature.
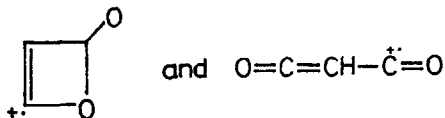
In the first decomposition step, which occurs in the temperature range 110–150°C, carbon monoxide is evolved:

$$\text{(I)}$$
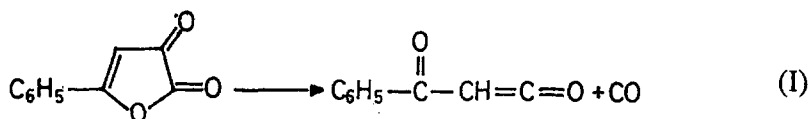
An equilibrium is probably set up between the cetene form of the product of reaction I and the lactone form [12]:
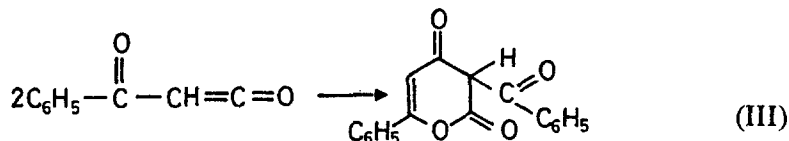

$$\text{(II)}$$
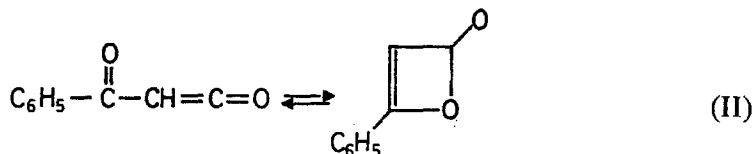
The mass-spectrometric data confirm the occurrence of reaction I, as the ions

($m/e = 69$) and $\overset{+\cdot}{C}\text{O}$ ($m/e = 28$) were identified.

The cetene form undergoes dimerization:

$$\text{(III)}$$

Such a dimer has been identified in the thermal decomposition in solution with benzene [3], mesitylene and bromobenzene [4].

The tendency of keto- and acylketenes to dimerize instead of cyclizing to oxetones in the gas phase has also been noted [5].

In the temperature range 150–220°C, the dimer undergoes decomposition, with the removal of benzaldehyde, as revealed by the thermogravimetric data and by the presence of the ion $C_6H_5-CO^+$ ($m/e=105$) in the mass spectrum.

The IR spectrum of the intermediate obtained when the heating was stopped at 220°C exhibited bands due to the carbonyl and monosubstituted phenyl groups, but did not allow an unambiguous determination of the molecular structure of the reaction product. The idea of an oligomeric species containing these groups may be considered [11, 13].

The first two decompositions steps overlap to a certain extent and cannot be resolved even by use of a heating rate of 2.5 K min^{-1}

The third decomposition step occurs in the temperature range 225–350°C. The thermogravimetric data indicate that in this step CO (from the carbonyl groups) is removed.

As seen from Fig. 1, this last step is kinetically feasible. Table 1 lists the values of the non-isothermal kinetic parameters (reaction order n, activation energy E and pre-exponential factor A) for CO removal.

Table 1 Values of non-isothermal kinetic parameters for the third decomposition step of

 at $\beta = 5$ K min^{-1}
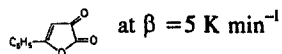
Kinetic parameters	Coats-Redfern	Flynn-Wall	Modified Coats-Redfern
n	1.4	1.4	1.3
E/kJ mol^{-1}	102	106	99
A/s^{-1}	5.1×10^6	1.6×10^7	2.91×10^6
r	–0.9986	–0.9988	–0.9987

r is the correlation coefficient of the linear regression.

Quite satisfactory agreement is observed among the values of the non-isothermal kinetic parameters.

The fractional value of the reaction order could be assigned to the decomposition of structural units consisting of various numbers of molecules.

Figure 2 shows the regenerated thermogravimetric curve in the coordinates α vs. T°C for the third decomposition step.

It can be seen from this Figure that the experimental points practically lie on the curve, thereby indicating the correctness of the determined values of the non-isothermal kinetic parameters, and of the approximations used in the applied integral method.
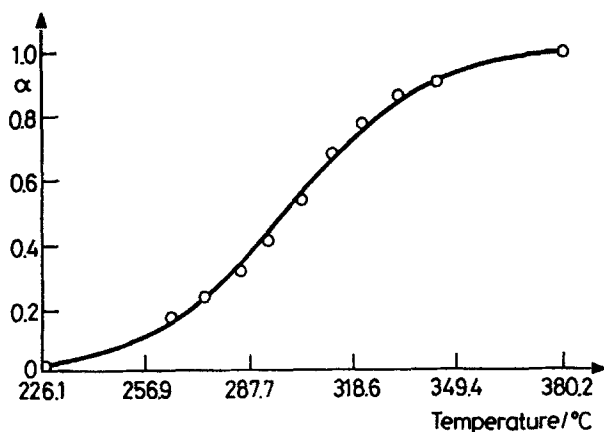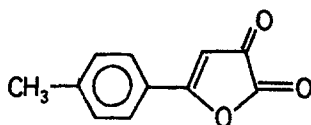
Fig. 2 Thermogravimetric curve regenerated in coordinates α *vs.* *T* °C by using the non-isothermal kinetic parameters obtained with the Coats-Redfern method for the third decomposition step of 5-phenyl-2,3-furandione. — calculated curve; o o o experimental points

Thermal decomposition of 5-(4-methylphenyl)-2,3-furandione
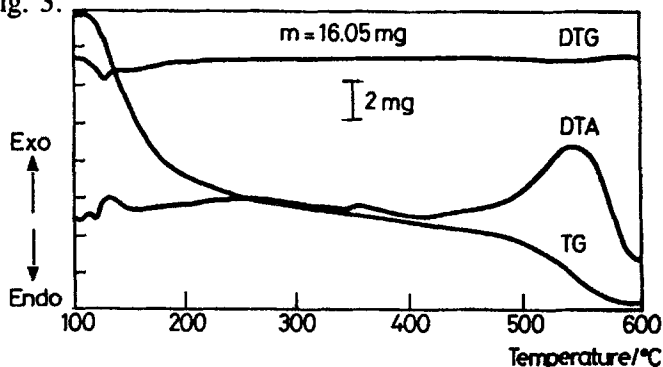## The thermal curves of the compound

is shown in Fig. 3.

Fig. 3 TG, DTG and DTA curves of 5-(4-methylphenyl)-2,3-furandione. *m* = sample mass
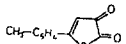
The thermoanalytical data coupled with the results of microscopic examination of the samples during heating show that the melting at 105°C occurs simultaneously with the decomposition. The first two decomposition steps take place similarly to those for 5-phenylfurandione.

The first decomposition step (CO elimination) occurs in the temperature range 105–145°C, whereas the second one, the removal of p-methylbenzoic aldehyde after dimerization, occurs in the interval 145–225°C. This mechanism is supported by the presence in the mass spectrum of the corresponding ions with $m/e = 28$ ($\overset{+}{C}O$),

m/e = 69   (+.⬚—O , +C—CH=C=O)

m/e = 91   (⬡—ĊH₂ , ⬡=CH₂ , ⬡)

m/e = 119   (H₃C—⬡—C⫰O⁺)
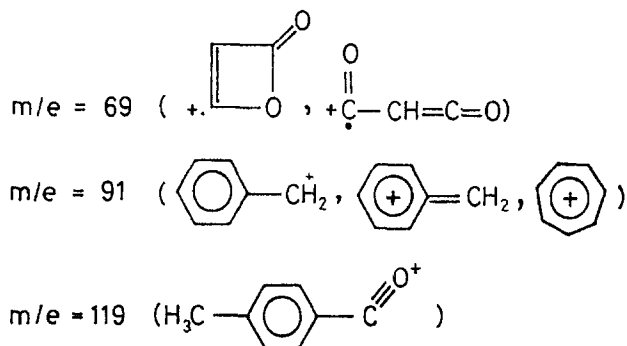
The IR spectrum of the decomposition intermediate obtained at 250°C exhibits bands corresponding to the carbonyl and disubstituted phenyl groups.

Table 2 lists the values of the non-isothermal kinetic parameters for the removal of p-methylbenzoic aldehyde in the second reaction step.
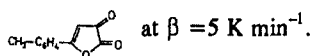
Table 2 Values of non-isothermal kinetic parameters for the second decomposition step of CH₃–C₆H₄–⬚ at $\beta = 5$ K min^{-1}.

Kinetic parameters	Coats-Redfern	Flynn-Wall	Modified Coats-Redfern
n	1.8	1.8	1.7
E/kJ mol^{-1}	66	70	64
A/s^{-1}	4.3×10^5	1.9×10^5	2.4×10^5
r	–0.9820	–0.9855	–0.9807

The values of the non-isothermal kinetic parameters obtained by the three applied integral methods exhibit quite satisfactory agreement. The reaction order close to 2 supports the idea that the removal of p-methylbenzoic aldehyde occurs mainly from a dimer.

In the temperature range 225–450°C, the resulting intermediate is quite stable. The slight weight loss recorded in the TG curve is due to vaporization of this compound. Its total oxidative degradation occurs in the temperature range 450–600°C. Evidence of the product of total degradation, CO_2, was observed in the mass spectrum of the heated sample.

The values for the nonisothermal kinetic parameters for this last decomposition step are given in Table 3.

Table 3 Values of non-isothermal kinetic parameters for the third decomposition step of

CH₃—C₆H₄—⟨structure⟩ at β = 5 K min⁻¹.

Kinetic parameters	Coats-Redfern	Flynn-Wall	Modified Coats-Redfern
n	1.0	1.1	1.0
E/kJ mol⁻¹	193	196	191
A/s⁻¹	9.2×10^9	1.4×10^{10}	7.2×10^9
r	−0.9983	−0.9985	−0.9982

The relatively good agreement among the values of the non-isothermal kinetic parameters determined by the three integral methods used, and the positions of the experimental points in the regenerated TG curve in the coordinates α vs. $T°C$ (Fig. 4) support the correct description of the experimental data by the model used and the applied procedures.
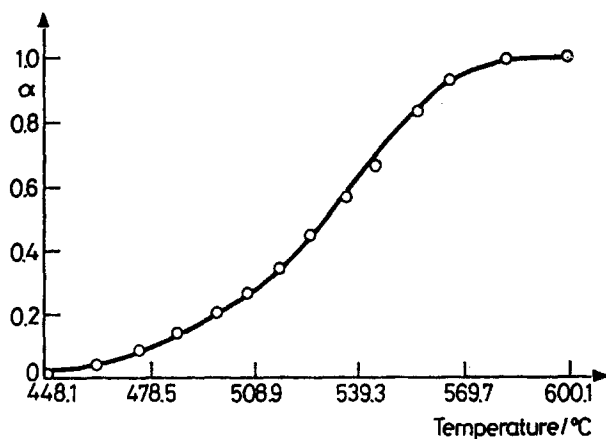

Fig. 4 Thermogravimetric curve regenerated in coordinates α vs. $T°C$ by using the non-isothermal kinetic parameters obtained with the Coats-Redfern method for the third decomposition step of 5-(4-methylphenyl)-2,3-furandione. — calculated curve; o o o experimental points

Thermal decomposition of 5-(4-chlorophenyl)-furan-2,3-dione

The derivatographic (Fig. 5) and microscopic data show that the decomposition occurs in the solid state.

The thermogravimetric data in the temperature range 120–160°C point to the evolution of CO_2:
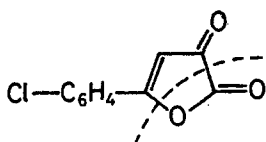
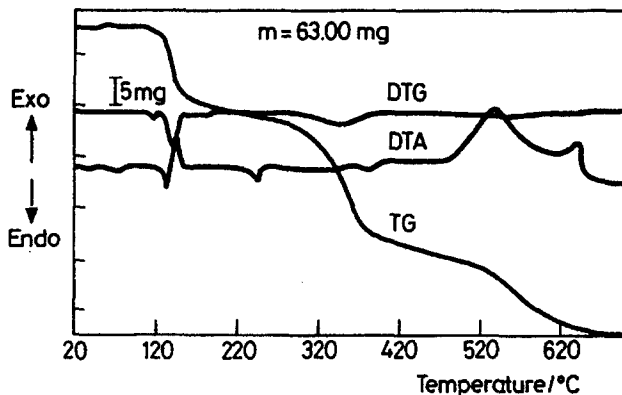Cl—C₆H₄—⟨structure⟩   (IV)

Fig. 5 TG, DTG and DTA curves of 5-(4-chlorophenyl)-2,3-furandione. m=sample mass

The mass spectrum of the evolved gas confirms the presence of CO_2. The IR spectrum of the intermediate obtained at 160°C contains bands corresponding to carbonyl- and disubstituted phenyl groups.

In the temperature range 160–270°C, the intermediate is stable (the IR spectra of the intermediates obtained at 160 and 240°C are identical). The endothermic peak at 245°C probably corresponds to the melting of the intermediate.

The values of the non-isothermal kinetic parameters for the first decomposition step are listed in Table 4.

Table 4 Values of non-isothermal kinetic parameters for the first decomposition step of

 at β =5 K min^{-1}.
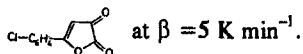
Kinetic parameters	Coats-Redfern	Flynn-Wall	Modified Coats-Redfern
n	1.1	1.1	0.9
E/kJ mol^{-1}	179	178	174
A/s^{-1}	3.2×10^{20}	1.7×10^{20}	7.02×10^{19}
r	–0.9944	–0.9968	–0.9441

As the value of the pre-exponential factor differs from that calculated via transition state theory ($\sim 10^{13}$ s^{-1}) [14], the value of close to unity obtained for the reaction order indicates an apparent order.

Figure 6 shows the regenerated thermogravimetric curve in the coordinates α vs. T°C for the first decomposition step.

The second decomposition step occurs in the temperature range 270–400°C. As shown by the DTG curve, the maximum decomposition rate is recorded at 350°C. The mass loss evaluated from the TG curve for the second step indicates
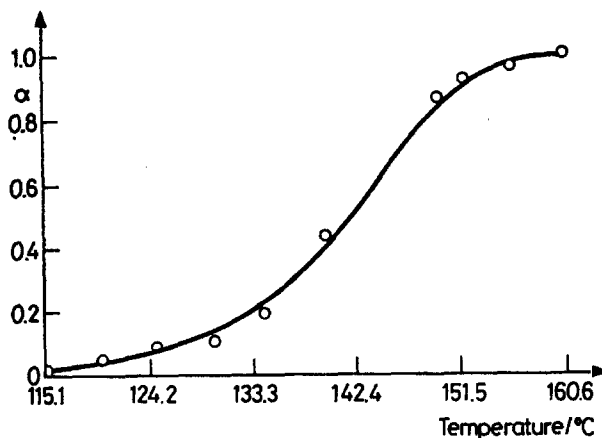
Fig. 6 Thermogravimetric curve regenerated in coordinates α vs. T °C by using the non-isothermal kinetic parameters obtained with the Coats-Redfern method for the third decomposition step of 5-(4-chlorophenyl)-2,3-furandione. — calculated curve; o o o experimental points

that probably the molecule $Cl-C \equiv C-CH=O$ is removed. The result is confirmed by the presence of the ion $Cl-HC=\overset{+}{C}=CH=O$ ($m/e=89$) is the mass spectrum.

Table 5 lists the values of the non-isothermal kinetic parameters for the second decomposition step.

**Table 5** Values of non-isothermal kinetic parameters for the second decomposition step of

 at β =5 K min^{-1}.
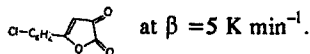
Kinetic parameters	Coats-Redfern	Flynn-Wall	Modified Coats-Redfern
n	1.1	1.1	1.0
E/kJ mol^{-1}	141.3	143.1	141.3
A/s^{-1}	2.49×10^9	4.41×10^9	2.44×10^9
r	–0.9987	–0.9989	–0.9984

When the order of magnitude found for the preexponential factor in taken into account, it can be appreciated that the n value of close to unity corresponds to a sterically hindered true monomolecular decomposition.

The residue obtained at 400°C undergoes oxidative degradation at higher temperature, the steps of which are rather difficult to separate. The IR spectrum of the intermediate obtained at 420°C reveals the loss of the bands corresponding to carbonyl and disubstituted phenyl groups.

Thermal decomposition of 4-benzoyl-5-phenylfuran-2,3-dione
As shown by the derivatogram of the compound (Fig. 7)
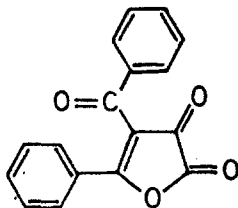
its thermal behaviour differs from that for the monosubstituted furan-2,3-dio-nes. The DTA curve demonstrates that the compound undergoes an endothermic change in the solid state at 70°C. This could be assigned to an isomerization, a transposition or a phase transition.

Comparison of the IR spectra of the initial compound and the intermediate obtained at 75°C indicates rather a *cis – trans* isomerization than a transposition [11].
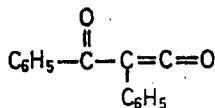
The first decomposition step occurs in the solid state, in the temperature range 100–160°C:

$$2CO + C_6H_5-C=\overset{\cdot}{C}-C-C_6H_5 \qquad (V)$$
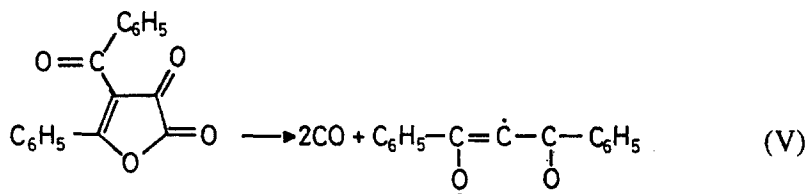
The resulting biradical can be stabilized either by dimerization to the cyclic dimer:
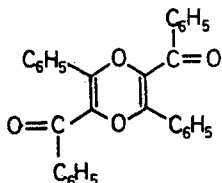
or by a transposition to the corresponding ketoketene

followed by dimerization as in the case of the 5-phenyl and 5-tolyl derivatives. The second possibility seems more probable [15].

The IR spectrum of the intermediate obtained at 170°C exhibits bands corre-sponding to carbonyl and monosubstituted phenyl groups and the mass spec-

trum indicates the presence of the ions $C_6H_5-C\equiv O^+$ ($m/e=105$), $C_6H_5-CO-\overset{+}{C}H-C_6H_5$ ($m/e=223$) and $C_6H_5^+$ ($m/e=77$), but no conclusive support for the real structure of the dimer is yet available.
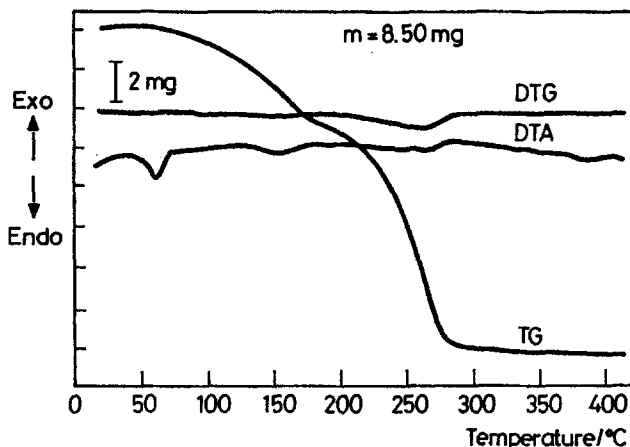

Fig. 7 TG, DTG and DTA curves of 4-benzoyl-5-phenyl-2,3-furandione. m=sample mass

The values of the non-isothermal kinetic parameters for reaction V are listed in Table 6 and the regenerated α vs. T °C curve is shown in Fig. 8.

Table 6 Values of non-isothermal kinetic parameters for reaction V

Kinetic parameters	Coats-Redfern	Flynn-Wall	Modified Coats-Redfern
n	2.4	2.3	2.3
E/kJ mol^{-1}	257	240	252
A/s^{-1}	1×10^{32}	7×10^{29}	2.8×1031
r	–0.9990	–0.9991	–0.9989

Despite the unusually high values of the pre-exponential factor, the obtained values of the kinetic parameters give a correct description of the experimental data (Fig. 8). However, the abnormally high preexponential factor values suggest that the non-isothermal kinetic parameters listed in Table 6 do not characterize chemical reaction V, being altered by physical limiting phenomena such as diffusion of the volatile component.

In the temperature range 175–280°C, the product of reaction V is totally removed.

In conclusion, this investigation of the thermal stability of some mono-and disubstituted furan-2,3-diones has furnished information concerning the decomposition steps which occur on progressive heating of the compounds, and also some structural evidence regarding the decomposition intermediates.
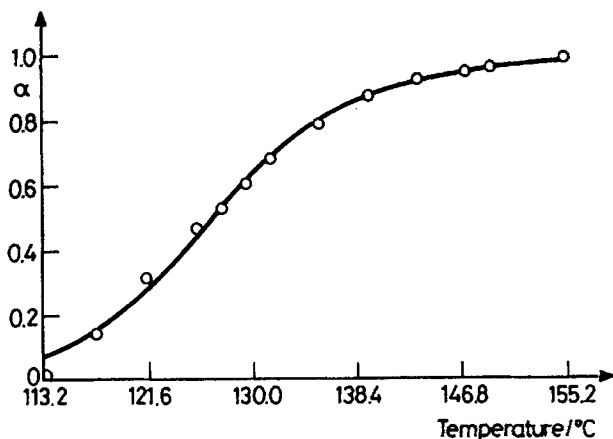
Fig. 8 Thermogravimetric curve regenerated in coordinates α vs. T °C by using the non-isothermal kinetic data obtained with the Coats-Redfern method for the third decomposition step of 4-benzoyl-5-phenyl-2,3-furandione. — calculated curve; o o o experimental points

For some of the reactions which occur in a single step, the evaluated non-isothermal kinetic parameters correlate satisfactorily with the structural data.

It may be inferred that a common feature of the first decomposition step for all the investigated derivatives is the breaking of the lactone ring, with elimination of CO or CO_2, depending less on the substituent at position 4 of the aromatic ring than on the solid/melted state of the starting compound.

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